

# PATENT SPECIFICATION

841,263

DRAWINGS ATTACHED



*Date of Application and filing Complete Specification: Aug. 7, 1956.*

*No. 24230/56*

*Application made in Germany on Aug. 4, 1955.*

*Complete Specification Published: July 13, 1960.*

Index at Acceptance:—Class 2(6), P7D1(A : X), P7(FX : K7), P7P(1A : 1B : 1C : 1F : 1X : 3 : 6A : 6B : 6X), P7T1C.

International Classification:—C08F.

## COMPLETE SPECIFICATION

### Process for polymerizing lower olefines in a continuous manner.

WE, FARBERWERKE HOECHST AKTIENGESSELLSCHAFT vormals Meister Lucius & Brüning, a body corporate recognised under German law, of Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement—

10 Proposals have been made concerning the preparation of high molecular polyethylene by polymerizing ethylene in the presence of a polymerization catalyst at atmospheric pressure or slightly above atmospheric pressure. Mix-  
15 tures of an aluminium-trialkyl compound with a salt of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, thorium or uranium are recommended as polymerization catalysts. The  
20 aluminium-trialkyl may be wholly or partially replaced by a compound of the general formula  $RA_2X_2$ , in which R is hydrogen or a hydrocarbon radical and X is a halogen or a hydrocarbon radical, each hydrocarbon radical  
25 having up to 8 carbon atoms. Dialkyl or monoalkyl halides are preferably used for this purpose. The exact composition of the polymerization activator is not known. Probably the metal salt undergoes reduction when it  
30 comes into contact with the aluminium compound.

By using different combinations of organoaluminium compounds with the salts of the aforesaid metals, it is possible to prepare  
35 catalyst systems having different activities, and it is advantageous to select for the polymerization of lower olefines with two or three carbon atoms, combinations which, on the one hand, ensure a favourable space time yield and, on the  
40 other, yield polymers having the desired

technological properties. For example, by the use of the system titanium tetrachloride-aluminium-ethyl sesquichloride ( $TiCl_4/Al(C_2H_5)_{1.5}Cl_{1.5}$ ) in a batchwise polymerization  
45 process (tank) for polymerizing ethylene, satisfactory space-time yields are obtained and the polymer satisfies the technological requirements. In the said polymerization process using titanium tetrachloride, which is reduced  
50 by the aluminium-ethyl sesquichloride, the space-time yield is about 40-50 kg. per cubic metre per hour.

As a measure of the molecular weight of the polyethylene, the value  $\mu$  spec./c determined in tetrahydronaphthalene at 120°C. is 2 to 6. The  
55 polymerization may be conducted in an aliphatic hydrocarbon, for example, an olefine-free petroleum distillate fraction, or in an aromatic hydrocarbon, for example, toluene or xylene, or in an alicyclic hydrocarbon, as dis-  
60 persion medium. The polymerization is carried out at 40-60°C., and in the case of small polymerization vessels, this temperature is established and maintained by means of a  
65 cooling jacket (heating jacket) that surrounds the reaction vessel.

In carrying out the polymerization by the batchwise process (Tank) the size of the reaction vessel is limited, on the one hand, because  
70 of the difficulty of removing heat of reaction from the thick mass of polymerization slurry in a large vessel and, on the other, because the introduction and distribution of the gaseous monomer become increasingly difficult as the  
75 polymerization proceeds, due to the lowering of the phase ratio of organic medium to polymerisate. Attempts have been made to overcome these difficulties by providing special  
80 cooling means in the form of tube-shaped cooling circuits that extend outside the reaction

[Price 3s. 6d.]

Price 4s. 3d. 5s. 0d.

vessel. However, the polymerization process penetrated into this cooling system and the tubes became rapidly clogged with solid polymer. It is also impractical to incorporate 5 the cooling system in the polymerization vessel, for this makes it difficult or impossible to remove the thick polymer slurry in a form free from residue. An external cooling jacket capable of removing the heat of polymerization 10 from the reaction vessel is effective only up to a certain tank capacity, due to the fact that the ratio of cooling surface to tank volume becomes unfavourable. Intense cooling with the use of cooling brine results in formation of a deposit 15 on the cooled wall and the polymerization rapidly ceases at the highly cooled places.

The present invention is based on the observation that lower olefines with two or three carbon atoms, i.e. ethylene or propylene or 20 mixtures of ethylene and propylene, can be polymerized in a continuous manner at atmospheric pressure or slightly raised pressure up to 30 atmospheres gauge at temperatures between +20°C. and 100°C., by continuously 25 circulating in a closed cyclic unidirectional tubular reaction system an organic medium containing at least one monomer with a catalytic amount of a two-component catalyst system consisting of a salt of an element of the 30 sub-groups IVA, VA or VI A of the Periodic Table and an organic aluminium compound. In the process of this invention the polymerization catalyst and the monomer are introduced into the cycle continuously or periodically, and 35 the resulting polymer dispersion is continuously withdrawn from the cycle.

Among the methods known for polymerizing ethylene under high pressure with the use of a peroxide catalyst, there are some in which the 40 polymers are produced in a continuous manner by introducing the gaseous monomer and activator admixed with the reaction medium continuously into a system of long pipes and simultaneously and continuously withdrawing 45 the polymer formed. In contradistinction thereto, the process of the present invention is carried out in a closed cycle with the use of the catalyst system mentioned in the opening part of this specification, whereby it is possible to 50 work without the application of pressure or under slightly superatmospheric pressure.

In the process of this invention it is of advantage to use a cyclic system in which the polymerization medium is circulated at a speed 55 of 5-10 metres per second by means of a high speed centrifugal pump. A suitable apparatus is shown by way of example in the accompanying drawing. In a cyclic pipe system 1, which is provided with cooling jackets 2, (the ratio of the cross-sectional area to the length of the pipe 60 may vary within wide limits, for example from 1:10 to 1:10,000, and is preferably 1:200).

A centrifugal pump 3, which operates, for example, at 3,000-5,000 r.p.m., circulates the 65 catalyst in admixture with organic medium.

The mixture of the catalyst combination and organic medium is introduced at a controlled rate by a piston pump at 4. The catalyst combination may be performed in a reactor and then introduced, or the components required to 70 forming the combination may be introduced individually, so that the catalyst combination is formed in the polymerization cycle or shortly before entering it.

The gaseous monomer is forced into the cycle 75 at 5 immediately in advance of the centrifugal pump 3, the amount introduced being controlled by means of a gas meter or rotameter. The polymer dispersion and the residual gas are continuously expelled from the upper part 80 of the cycle through a pipe 6, and degassing takes place in the pipe 6 and the gas is expelled at 7. The dispersion passes into a receiver 8, from which it is withdrawn for further treatment. The residual gas is returned to the 85 cycle by way of pipe 9, or it may be blown off.

The residence time of the reaction mixture in the cycle depends on the volume of the cycle and of the mixture of catalyst and organic 90 medium introduced, and may be, for example, from 1 to 10 hours. The ratio of polymer to organic medium, which may vary from 1:2 to 1:20, depends on the amount of monomer introduced into the organic medium 95 per unit time. The desired polymerization temperature, which may be, for example, within the range of +20°C. to +80°C., is maintained by means of the cooling or heating jackets 2. 100

It is known that in carrying out chemical reactions with the use of catalysts, it is necessary, when the reactants are moved at a high speed, to use a catalyst of which the activity is sufficiently high. 105

Therefore, in carrying out the process of the invention, care should, of course, be taken to adjust the speed of circulation (for example, from 0.3 to 10 metres/sec.) and the withdrawal of polymer dispersion from the cycle 110 in accordance with the activity of the catalyst mixture. In the case of a catalyst system of low activity, it is advantageous not to move the reaction mixture too rapidly through the cycle, and it is sometimes advantageous to introduce, 115 at any desired point of the cycle, components which will reactivate the catalyst system.

As stated above, there are many possible combinations of metal salts, e.g. of the titanium group with organo-aluminium compounds 120 from which can be prepared an activator system having an activity suited to the polymerization system. Thus, in the case of the above described rapidly moving cyclic polymerization system, the combination of titanium 125 tetrachloride with an aluminium-trialkyl (for example, in a ratio of 1:0.1 to 1:12) is a suitable activator system which possesses a sufficiently high activity and leads to polymers having molecular weights within the range 130

suitable for technical application.

The process of this invention constitutes a considerable improvement in the technique of polymerization. The resulting polymers are obtained with great uniformity of reaction and molecular weight, and the space-time yields exceed those obtained by the batchwise method of polymerization.

The following Example illustrates the invention:

25 millilitres per minute of a solution of 10 millimols of titanium tetrachloride per litre and 15 millimols of aluminium-triethyl per litre, both compounds being dissolved in an olefine-free petroleum distillate fraction boiling at 200-220°C., were introduced by means of an accurately working piston pump into a cyclic pipe of 3 litres capacity. Before entering the closed cycle the two catalyst components and the solvent were mixed together in a pipe the length of which was such that the residence time of the catalyst formed was about 2 minutes. As soon as the cyclic pipe, from which the air had been displaced by dry nitrogen before the beginning of the experiment, was filled, a centrifugal pump, which was inserted in the cyclic pipe, was operated so as to circulate the reaction medium at a speed of 7.5 metres per second. The polymerisation temperature was regulated by means of a heating jacket, which surrounded the polymerisation cycle and through which water at 50°C. flowed in order to maintain this temperature in the reaction tube. As soon as the cyclic tubular reaction system was filled 220 litres of ethylene were introduced per hour. The polymerization which took place under atmospheric pressure, set in immediately and the polymer dispersion passed from the overflow into a receiver, from which it was withdrawn. The polymer dispersion was worked up in the usual manner by filter-

ing off the polymer and washing the latter with acid and alkali and drying it. The conversion was 100%. The polymer had a viscosity of  $\mu \text{ spec./c} = 3.2$ . The ratio of polymer to organic medium may be reduced, if desired, to the limit of pumpability by increasing the amount of ethylene introduced.

#### WHAT WE CLAIM IS:

1. In the process for polymerizing or copolymerizing lower olefines with two to three carbon atoms by contacting an organic medium containing at least one monomer with a catalytic amount of a two-component catalyst system which consists of a salt of an element of the sub-groups IV-A, V-A or VI-A of the Periodic Table and an organic aluminium compound, the improvement which comprises continuously circulating the mixture of at least one monomer, the catalyst and the organic medium in a closed cyclic unidirectional tubular reaction system as described herein, at atmospheric or slightly raised pressure up to 30 atmospheres gauge, at temperatures between +20°C. and 100°C. and continuously withdrawing the resulting polymer dispersion from said system.
2. A process as claimed in Claim 1, wherein ethylene is polymerized.
3. A process as claimed in Claim 1, wherein propylene is polymerized.
4. A process as claimed in Claim 1, wherein a mixture of ethylene and propylene is polymerized.
5. A process for polymerizing a lower olefine, conducted substantially as described in the Example herein.
6. Polyolefines whenever made by the process claimed in any one of Claims 1-5.

ABEL & IMRAY

Agents for the Applicants,  
Quality House, Quality Court, Chancery Lane,  
London W.C.2.

